



Original research paper

Geochemical characteristics of terrestrial shale gas and its production prediction significance in the Ordos Basin, China[☆]

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Abstract

In order to study the variation of shale gas composition as well as the carbon isotopic fractionation characteristics of terrestrial shale in the Ordos Basin, and ultimately establish a prediction model for shale gas production in order to monitor production capacity and effectively manage the development of shale gas, selected core samples from production wells were obtained for desorption analyses of their corresponding gas composition and carbon isotope. The desorption results showed that the methane content of the desorption gas is relatively low, the drying coefficient (C_1/C_{1-5}) ranges from 0.6 to 0.8, and the carbon isotope is relatively negative compared to other places. By means of the increasing desorption and production time, the drying coefficient and carbon isotope values of such samples show obvious carbon fractionation during gas adsorption/diffusion processes. The changes are more evident with increasing heavy hydrocarbons (C_{2+}) and heavier carbon isotope values. The drying coefficient shows good correlation ($R^2 > 0.8$) with the content of shale gas desorption per unit mass. A gas production prediction model was proposed to predict gas production throughout the life of the production well based on the relationship between the drying coefficients and gas production volume in the Ordos Basin.

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Keywords: Terrestrial shale; Gas component; Carbon isotope; Gas production prediction model

1. Introduction

Gas component and stable carbon isotope value serve as key geochemical parameters to the research generation. The elimination and migration of hydrocarbon are of extensive significance in identifying the types of natural gas genesis,

defining maturity of organic matters, and contrasting oil-gas sources [1–6]. Substantive simulation experiment results and onsite observed data by predecessors show that: in the course of migration of conventional gas in the formation pore system, understandable fractionation effect that occurs in carbon isotope, which, to be specific, is shown in preferential migration of methane relative to heavy hydrocarbon, isomeric butane relative to normal butane, and light carbon isotope relative to heavy carbon isotope [7–10]. The reasons behind this are differences in the chemical reaction activate energy, mass number, molecular structure or adsorbability of different components or different isotopic molecules in a generation, migration, and lastly, the preservation or dissipation course of natural gas [10,11]. As a non-conventional hydrocarbon

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resource, shale gas is characterized by self-generation and self-storage relative to the conventional gas reservoir. Generally, it does not migrate nor does it diffuse over a long distance, its component and carbon isotopic fractionation characteristics are more likely to be greatly different from those of conventional gas.

Research performed by predecessors believe that gas diffusion and adsorption are the major factors which influence migration of gas in shale or other tight stratum origins, making the gas generate components and stable carbon isotopic fractionation [6,9–11]. The main cause for gas diffusion to result in component and carbon isotopic fractionation is that methane is relative to heavy hydrocarbon, and light carbon isotope component is relative to heavy carbon isotope component, it has higher diffusibility that eventually causes gas components to be dampened and carbon isotope value to be on the negative side. The predecessors performed diffusion and analysis experiment on dry shale to find whether the gas diffusion front obviously abounded in the ^{12}C -methane and whether the migrated methane carbon isotope value could reduce by 30‰ [12,13]. Meanwhile, water-saturated shale can also cause large carbon isotopic fractionation generated in diffusion process of methane [6]. Some scholars have explored carbon isotopic fractionation model caused by gas diffusion migration [14–16].

The adsorption of clay minerals and organic matters for gasses will also lead to fractionation of stable carbon isotope. However, this has been barely delved into comparatively [17,18]. Fuex [17] conducted a methane adsorption experiment using a high polarity chromatography column. He found out that this chromatography column had lower affinity to non-polarity methane and that the carbon isotopic fractionation was smaller than 1‰. Gunter [18] conducted the same experiment using a 13 Å molecular sieve whose methane adsorptivity was stronger in finding out whether the methane carbon isotopic fractionation caused by adsorption could exceed 10‰. As the chromatography column was applied in the experiment it's characterized by dryness and high specific surface area compared to formation shale sample. It is hard to contrast the influence of adsorption displayed by the experimental result on methane isotope with a practical situation. However, at least the experimental result can validate possible influence of adsorption on carbon isotopic fractionation.

Lu [19] collected fresh shale core on top of the gas reservoir, measured the components of residue gas and carbon isotope value. Lu found out that the methane carbon isotope value at this position (from -36.6‰ to -25.5‰) was far larger than the counterpart in the reservoir (-41.9‰). It also increased as the depth became more sizeable; it was unrelated to physical properties of rocks and minerals characteristics. The research believed that the change of methane carbon isotope was primarily influenced by gas diffusion and clay mineral adsorption. Xia [16] considered gas adsorption and diffusion process and raised a gas continuous flow model to simulate isotopic fractionation phenomenon caused by migration of natural gas in coal and shale. This author believed that the early migration after gas generation would turn the

carbon isotope to the negative side due to the strong adsorptive capacity of hydrocarbon source rock.

Han et al. [20] analyzed gas components and characteristics of carbon isotope as well as desorbed shale gas on site to discover that the ethane content increased regularly with the increase of desorption time in the desorption process of shale gas; the $\delta^{13}\text{C}_1$ value increased to a certain extent. Meanwhile, a handful simulation experiments on coal-seam gas also saw that the methane carbon isotope value increases with the surge of desorption time [21–23]. Gao et al. [24] analyzed basic geochemical characteristics of desorbed gas from the Upper Triassic shale in the Junggar Basin, it is generally thought that the shale gas in this region was dry gas with low carbon isotope value, exhibiting characteristics of the conventional low maturity situ sapropel type natural gas. Du et al. [25] analyzed components and carbon isotope and formulated that shale gas in the Yanchang Formation in the southeast of the Ordos Basin was dominated by pyrolyzed moisture. Additionally, the carbon isotope series was basically positive basically indicating that there's idiogenous gas was mixed in this segment.

To sum things up, current research on the components of natural gas and characteristics of carbon isotope in a non-conventional compact reservoir is mainly focused on describing basic geochemical characteristics, fractionation mechanism, and gas genesis, etc. There's deficient research on the correlation between the desorbed gas amount of shale or per well rate and geochemical change characteristics of. Thus, the paper collected onsite desorbed gas and gas sample from trial-producing well and analyzed components and carbon isotope, subsequently combining field data of production well to establish an effective single well shale gas yield prediction model to provide a useful reference for shale gas reserve estimate and dynamic monitoring of productive capacity.

2. Sample and experiment

2.1. Geologic background and sample

Mainly located in the southeast of the Yishan slope in the Ordos Basin, the researched area has a gentle structure with a strata dip of $<1^\circ$. The main body is located in the Yan'an city within Shaanxi Province (Fig. 1a). The Mesozoic Ordos Basin experienced multistage sedimentation, polycyclic uplifting and reconstruction, and several other sedimentary cycles [26–28]. Thereunto, the Upper Triassic series in the Yanchang Formation is just a limnetic facies which the clastic successions series developed in the stable sedimentation period. The section Chang 7 has lithologic characters of mainly dark-colored shale, carbargilite, oil shale with the thickness being 70–150 m. Section Chang 7 is the main exploration target formation layer of hydrocarbon source rock and shale gas (Fig. 1b).

2.2. Experimental method

The research samples were mainly onsite shale desorbed gas sample. The onsite desorption of shale gas requires the

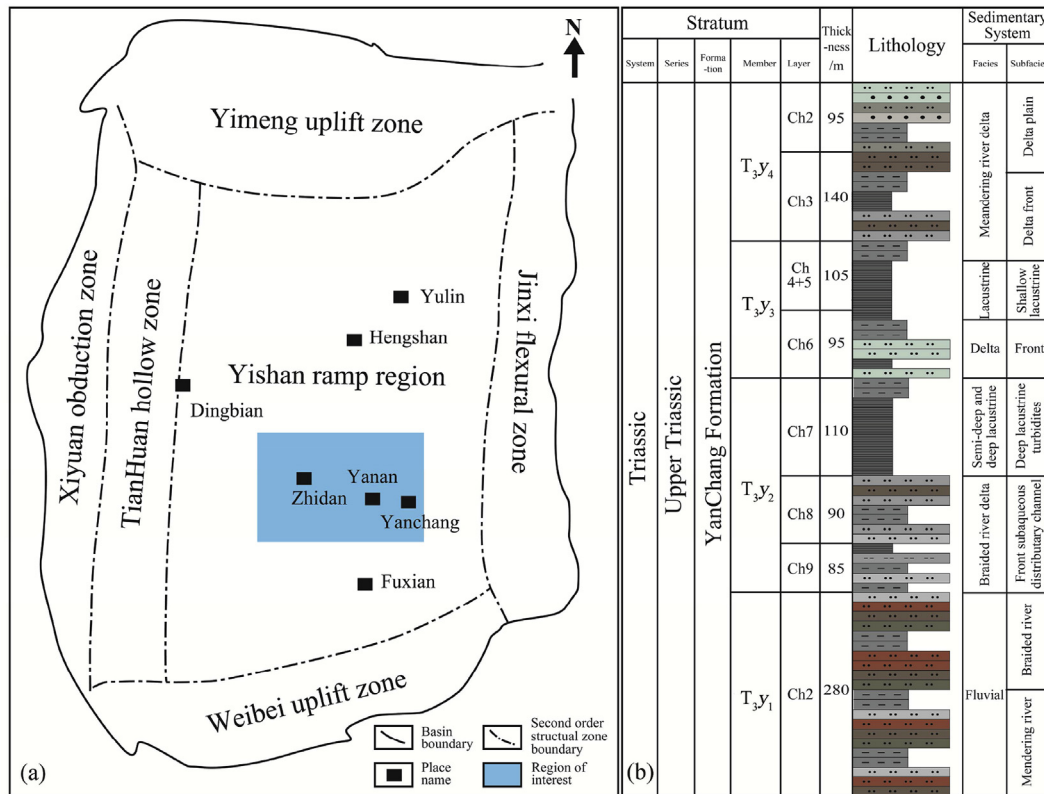


Fig. 1. Location of the study area and its stratigraphic chart.

immediate placing of the sample into the desorption pot filled with the saturated saline solution used to seal the core after it has been taken out. The saturated saline solution in the desorption pot and the constant-temperature water tank should be heated in advance to the temperature of the corresponding core layer and the temperature should be unceasing (for example the temperature gradient of the formation where the core well is located this time is 2.5 °C/hm, coring depth of the core is 1308–1352 m, external temperature is 23 °C, and the corresponding formation temperature is set to 55 °C). Then desorption pot is then placed in a constant-temperature water tank, and the desorption pot valve and inversion measuring cylinder are connected by a conduit (Fig. 2). Usually, only a small amount of gas is precipitated after 4 h post core desorption at a constant temperature under formation temperature, then desorption temperature was gradually increased to 95 °C, then desorption at a constant temperature last for 3–4 h till the end of the desorption.

In the course of desorption at a constant temperature, a rubber tube was utilized to lead the desorbed gas into measuring cylinder, and metered desorbed gas at fixed time node; used a funnel to lead desorbed gas into a gas-sample bottle whose air was already exhausted from measuring cylinder time piecewise. After the sample collection, we respectively used Agilent 6890N GC gas chromatograph and Thermo Scientific TRACE GCULTRA-GC ISOLINK-MAT 253 IRMS to analyze gas components and stable carbon isotope. Related experiments were all conducted in a national

key lab of hydrocarbon resources and detection of the China University of Petroleum.

3. Result and discussion

3.1. Desorbed gas components

3.1.1. Basic characteristics of gas components

The result of experimental analysis on components of onsite desorbed gas showed that (Table 1), the content of CH₄, C₂H₆, and C₃H₈ in the components of desorbed gas mainly

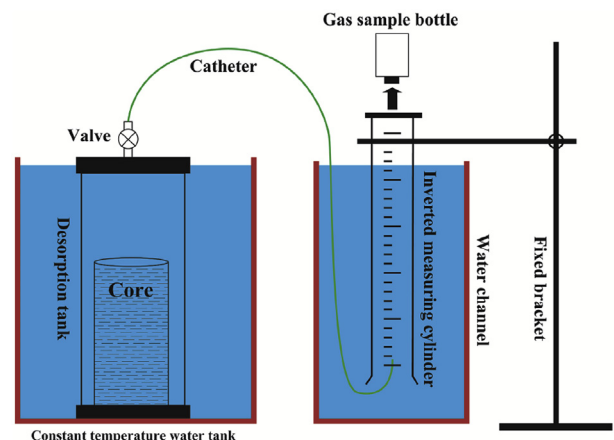


Fig. 2. Diagram of desorption and collection of shale gas.

Table 1
Carbon isotope compositions of the desorbed gas in the Well YY-22.

Sample	Time/h	Gas content/ml	Carbon isotope/‰							
			C ₁	C ₂	C ₃	iC ₄	nC ₄	iC ₅	nC ₅	CO ₂
YY22-8a	0.5	180	−51.0	−34.2	−31.0	−34.3	−31.0	−30.3	−31.5	−15.1
YY22-8b	1	266	−51.5	−34.4	−31.0	−34.1	−31.0	−30.2	−31.7	−14.2
YY22-8c	4	468	−50.8	−34.5	−31.1	−34.5	−31.3	−30.5	−31.5	−13.5
YY22-8d	8	760	−48.0	−33.9	−31.0	−34.4	−31.1	−30.5	−31.5	−13.5
YY22-9a	1	150	−51.7	−34.7	−31.2	−34.4	−31.5	−30.9	−31.7	−16.6
YY22-9b	4	278	−52.1	−35.0	−31.5	−34.7	−31.6	−30.9	−31.6	−15.2
YY22-9c	8	576	−48.2	−34.5	−31.6	−34.8	−31.6	−31.0	−32.0	−14.6
YY22-14a	0.5	282	−50.9	−34.2	−31.2	−34.7	−31.4	−30.2	−31.8	−15.9
YY22-14b	1	388	−50.5	−34.3	−31.2	−34.9	−31.3	−30.0	−31.9	−14.6
YY22-14c	2	500	−49.0	−34.0	−31.2	−35.0	−31.4	−30.2	−31.8	−15.6
YY22-14d	4	586	−47.4	−33.6	−31.2	−34.9	−31.2	−29.9	−31.8	−14.8
YY22-14e	7	782	−45.6	−32.9	−31.1	−35.0	−31.3	−30.1	−31.6	−15.1
YY22-15a	0.5	464	−50.8	−34.0	−31.1	−34.8	−31.2	−30.0	−31.6	−14.5
YY22-15b	1	594	−50.4	−34.2	−31.3	−35.0	−31.3	−29.8	−31.9	−15.4
YY22-15c	2	716	−48.4	−33.8	−31.1	−34.9	−31.1	−29.9	−31.7	−14.4
YY22-15d	4	804	−46.7	−33.4	−31.1	−34.9	−31.2	−29.9	−31.5	−14.5
YY22-15e	7	962	−44.6	−32.5	−30.8	−35.0	−31.1	−30.0	−31.6	−14.7
YY22-20a	1	546	−50.5	−34.6	−31.5	−35.2	−31.5	−30.1	−31.8	−14.7
YY22-20b	2	662	−48.9	−34.3	−31.5	−35.0	−31.4	−30.2	−31.6	−14.3
YY22-20c	4	736	−47.6	−34.0	−31.3	−35.1	−31.3	−30.0	−31.8	−14.8
YY22-20d	8	954	−40.9	−32.5	−31.1	−35.2	−31.3	−30.1	−31.6	−15.2
YY22-21a	1	472	−50.3	−34.6	−31.4	−35.1	−31.4	−30.0	−31.8	−14.1
YY22-21b	4	592	−48.6	−34.4	−31.5	−35.1	−31.4	−30.1	−31.8	−15.3
YY22-21c	8	730	−39.7	−32.7	−31.1	−35.0	−31.2	−30.0	−31.6	−16.5
YY22-26a	0.5	656	−52.2	−35.5	−32.0	−35.1	−31.6	−30.7	−32.1	−15.3
YY22-26b	2	912	−48.1	−35.3	−32.4	−35.3	−31.8	−30.9	−32.2	−14.7
YY22-26c	4	974	−45.4	−34.7	−32.1	−35.2	−31.8	−30.8	−32.0	−15.6
YY22-26d	8	1233	−43.4	−34.3	−32.2	−35.3	−31.8	−31.0	−32.1	−14.2
YY22-27a	0.5	344	−53.0	−34.9	−31.5	−35.2	−31.4	−30.2	−31.8	−15.5
YY22-27b	2	568	−50.7	−34.8	−31.6	−35.2	−31.6	−30.3	−31.9	−14.7
YY22-27c	4	662	−48.4	−34.2	−31.2	−34.8	−31.3	−30.8	−31.8	−13.8
YY22-27d	8	824	−45.3	−33.6	−31.3	−35.2	−31.4	−30.1	−31.8	−14.7
YY22-32a	0.5	406	−51.5	−35.8	−32.5	−35.0	−31.9	−30.8	−32.4	−15.6
YY22-32b	1	510	−49.9	−35.6	−32.6	−35.3	−32.0	−30.8	−32.3	−14.6
YY22-32c	4	650	−46.5	−34.8	−32.3	−35.3	−32.0	−30.9	−32.3	−15.5
YY22-32d	7	803	−43.0	−33.7	−32.1	−35.2	−31.9	−30.7	−32.0	−14.0

ranged from 55% to 78%, 10% to 18%, and 4% to 10%. The volume fraction of iC₄ and nC₄ was 1%–5%, whereas the composition percentage of iC₅ and nC₅ was 0.5%–2%. The gas drying coefficient (C₁/C_{1–5}) mainly ranged from 0.6 to 0.8, the value of C₁/C₂₊₃ was mostly smaller than 5; this indicated the drying coefficient of shale gas in this area was on the low side, methane content was relatively low, heavy hydrocarbon content was comparatively high, and moisture dominated.

3.1.2. Gas components fractionation

We collected onsite desorbed gas time piece wisely. Then the gas components were analyzed, and the component fractionation characteristics in the desorption process of shale gas were explored. The experimental result showed that the increase of desorption time, the methane content decreased constantly by 15% to over 40% (Fig. 3a). The content of heavy hydrocarbon component (C₂₊) increased constantly with the increased desorption time. There is a positive correlation between the two. The increased rates of ethane and propane are

the greatest, reaching a maximum up to 10% (Fig. 3b–e). The gas drying coefficient of C₁/C_{1–5} and C₁/C₂₊₃ decreased significantly with the desorption time, indicating the escalation of shale desorption time and desorbed gas amount, the proportion of methane declined, the content of heavy hydrocarbon component increased, and the gas was dampened gradually (Fig. 4a and b).

Research performed by predecessors believed that the main reason that caused fractionation is the gas components that influenced adsorption/diffusional effect, molecular weight, molecular diameter, and solubility coefficient of methane were insignificant relative to the heavy hydrocarbon. Thus, the methane's capacity of being adsorbed by rock minerals was weak, whereas the diffusion coefficient was great, resulting eventually in preferential precipitation of methane compared to other heavy hydrocarbon components in the course of shale desorption [9,10]. As desorption proceeded, the relative percentage composition of methane declined, while volume fraction of ethane and propane increased accordingly. Especially after desorption temperature ascended from 55 °C to

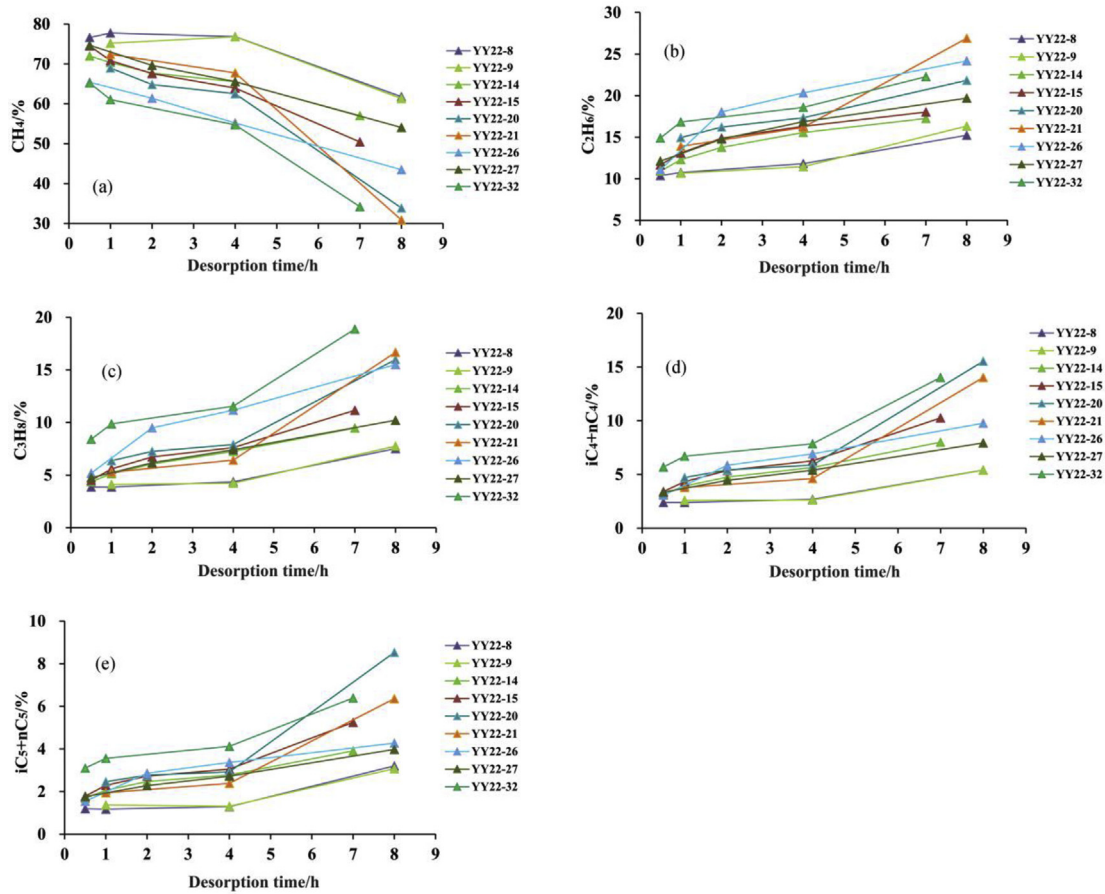


Fig. 3. Relationship between the content of gas components and desorption time.

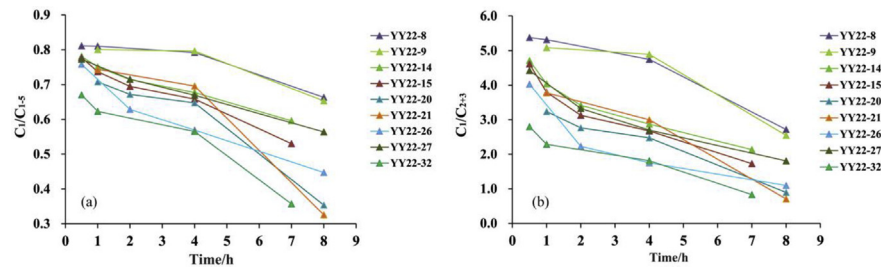


Fig. 4. Relationship between the drying coefficient and desorption time.

95 °C, the content of heavy hydrocarbon component showed a substantial increase.

3.1.3. Gas component and desorbed gas amount

To explore the correlation between the shale gas component and desorbed gas amount, the paper plotted a graph (Fig. 5a and b) of the relationship between the desorbed gas drying coefficient (C_1/C_{1-5} , C_1/C_{2+3}) and the desorbed gas amount of unit mass (ml/g). The results showed a satisfactory correlation and linearly dependent coefficient is $R^2 > 0.8$.

According to the association between gas component drying coefficient and desorbed gas amount per unit shale mass, we can attempt to establish a prediction model of shale air content. As shown in Fig. 5, the logarithmic graph of the

relationship between the drying coefficient (C_1/C_{2+3}) and desorbed gas amount per unit mass shows the logarithmic correlation coefficient of the two is greater than 0.8. Based on this, we assumed that the methane in shale was completely desorbed, subsequently, the drying coefficient (C_1/C_{2+3}) will approach 0. At this moment, the junction of the logarithmic curve production (broken line) and the X-axis are the largest accumulative desorbed gas amount by per gram of shale sample. By combining the spatial distribution of shale abounding in organic matters in the researched area and actual recovery of shale gas, we can make a preliminary prediction of the shale gas yield in this region. In the same manner, by way of the relationship between the per well rate and a gas component known, productive capacity of shale gas can be

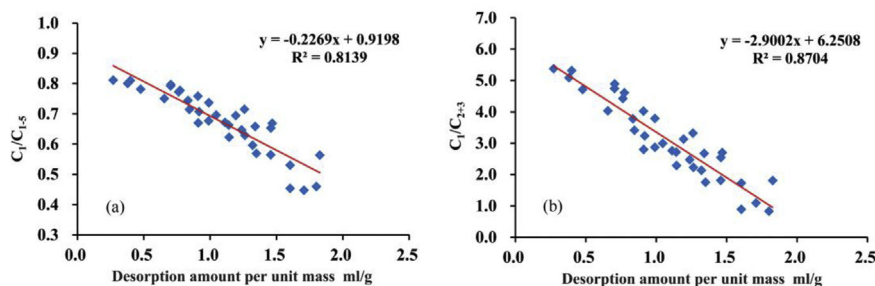


Fig. 5. Relationship between the drying coefficient and the content of unit mass desorbed gas.

monitored in a dynamic way by regularly testing change of gas components.

However, it is noteworthy that the actual formation is largely different from the desorption experiment condition. Most especially the site desorption experiment pressure is largely different from the actual pressure in the formation. Hence, some scholars placed forward that gas diffusion and migration might cause large gas component and isotopic fractionation when the lab was fully degasified. Nonetheless, in actual geological conditions, corresponding fractionation effect is comparatively limited (<5‰) [16]. Thus, to establish this prediction model, change of gas component in the production well and monitoring data of yield of production well need to be corrected.

3.2. Carbon isotope of desorbed gas

3.2.1. Carbon isotope characteristics

The analysis result on the carbon isotope of desorbed gas from shale showed that (Table 1) the distribution range of carbon isotope value for CH₄, C₂H₆, and CO₂ was from −53.0‰ to −39.7‰, −35.8‰ to −32.5‰ and −16.6‰ to −13.5‰, respectively. The carbon isotope values for C₃H₈, iC₄, nC₄, iC₅, and nC₅ firmly ranged around −31.5‰, −35.0‰, −31.5‰, −30.5‰, and −31.8‰. From the value distribution of carbon isotope in gas components, it is observed that the shale gas in this region is organic in origin. The carbon isotope value for the initially desorbed CH₄ and C₂H₆ was on the negative side, indicating that the shale maturity in the researched area is relatively low.

3.2.2. Carbon isotopic fractionation

The correlation graph of the carbon isotope value and desorption time was established according to the measurement of carbon isotope achieved in the desorbed gas (Fig. 6). The graph shows that both the $\delta^{13}\text{C}_1$ and $\delta^{13}\text{C}_2$ increase constantly with the longer desorption time, indicating in desorption course of shale gas, shale can obviously fractionate carbon isotope of CH₄ and C₂H₆. The carbon isotope values for the two all have varying weight increase. Hereinto, the carbon isotope value for CH₄ has a large change in weight, up to above 10‰ maximally (Fig. 6a), while the weight change of carbon isotope value for C₂H₆ is about 2‰ (Fig. 6b). The distribution of carbon isotope value for other heavy

hydrocarbon components (C₃H₈, iC₄, nC₄, iC₅ and nC₅) is stable without significant weight increase despite the longer desorption time.

The diffusion effect serves as the main reason for carbon isotopic fractionation in production or desorption of shale gas [12–16]. In comparison to light isotope, the heavy isotope of one component has a larger molecular radius and smaller diffusion coefficient, therefore, the light isotope is generally diffused and migrated. The kinematic explanation states that precipitate molecule containing ¹³C needs more energy than precipitate molecule containing ¹²C in the same component [29,30]. Thus, as desorption takes place and the desorption temperature increases, the content containing heavy isotope ¹³C rises accordingly and desorbed gas becomes heavy gradually. In addition, tight rocks, such as shale, etc., have relatively strong gas adsorption ability, thus, some scholars believed that adsorption of rock mineral also had a certain effect on fractionation of gas carbon isotope [16,19].

3.2.3. Carbon isotope and desorbed gas amount

By establishing the relationship between the gas carbon isotope value ($\delta^{13}\text{C}_1$, $\delta^{13}\text{C}_2$) and the desorbed gas amount per unit mass shale (ml/g) (Fig. 7), the correlation between $\delta^{13}\text{C}_1$ and desorbed gas amount per unit mass will be relatively good, not to mention, the linearly dependent coefficient R^2 approaches 0.7 (Fig. 7a); while the correlation of $\delta^{13}\text{C}_2$ remains relatively bad at $R^2 < 0.2$ (Fig. 7b). Likened to drying coefficient of the gas component, the general correlation between carbon isotope value and desorbed gas amount remained unsatisfactory, which may be related to measuring the error in carbon isotope experimental analysis.

Some scholars found a good positive correlation between “inverted sequence” degree of carbon isotope and gas content of shale [19–21]. Tilley [31] thought that the phenomenon of “inverted sequence” of the isotope showed shale was in a relatively closed state and could be preserved well. Thus, the higher the degree of “inverted sequence” of the isotope, the higher the gas content. Xia [32] thought the main reason for “inverted sequence” of isotope was: liquid hydrocarbon pyrolysis gas that was abundant in more heavy hydrocarbon components than kerogen pyrolysis gas in high maturity stage, composition of carbon isotope was relatively light, and when CH₄ from kerogen pyrolysis gas was mixed with C₂H₆ from liquid hydrocarbon pyrolysis gas, the “inverted sequence” of

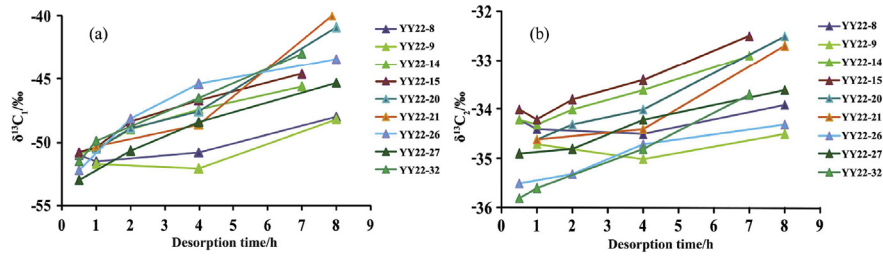


Fig. 6. Relationship between the $\delta^{13}\text{C}_1$, $\delta^{13}\text{C}_2$, and desorption time.

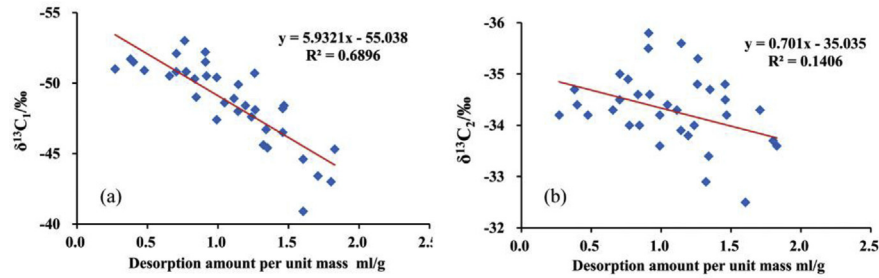


Fig. 7. Relationship between the $\delta^{13}\text{C}_1$, $\delta^{13}\text{C}_2$, and the content of unit mass desorbed gas.

$\delta^{13}\text{C}_1 > \delta^{13}\text{C}_2$ appears. However, the result of the experimental analysis in this paper showed that in general $\delta^{13}\text{C}_1$ is much less than $\delta^{13}\text{C}_2$. There is no phenomenon of “inverted sequence” of isotope (Table 1). The general maturity of shale in the researched area was on the low side, and kerogen did not reach high maturity stage of pyrolysis; it did not generate substantive CH_4 . Thus, the CH_4 and C_2H_6 in the desorbed gas are mainly from pyrolysis of liquid hydrocarbon.

3.3. Gas component and carbon isotope in the production well

According to the analysis result of the onsite desorption of shale core, we preliminarily estimated that the gas component and the effect of carbon isotopic fractionation are supposed to also exist in fracturing recovery process of shale reservoir, i.e. the component and carbon isotope value of shale gas produced by the same well in different production periods and brought in well of different periods in the same period are supposed to be differing. Basic change trend is estimated to be: the heavy hydrocarbon component in gas increases and carbon isotope gains weight with an increase of production time.

Based on the aforementioned estimation, we assumed that the gas amount produced in a single well is proportional to time. After collecting the gas sample of one same objective section of brought in well in different periods, measuring gas component content, and carbon isotope value, and establishing relation between gas drying coefficient, methane carbon isotope value and production time of production well (Fig. 8), we can get the relationship between the component and carbon isotope value of gas in production well and produced gas amount. Analytical result showed that in comparison with the desorbed gas, the content of gas component CH_4 in production well mainly ranged from 66.4% to 77.5%, carbon isotope values of CH_4 and C_2H_6

were respectively concentrated at -51.2‰ to -47.4‰ and -37.0‰ to -38.7‰ (Tables 2 and 3), these indications were compared with onsite desorption result. The CH_4 content in shale gas component in actual formation was relatively higher, carbon isotope value was relatively lighter, and fractionation effect was relatively small. Correlation between the content of component and carbon isotope value of gas in the production well and production time was good, the coefficient of correlation of gas drying coefficient is $(\text{C}_1/\text{C}_{1-5}, \text{C}_1/\text{C}_{2+3}) R^2 > 0.9$ (Fig. 8a and b). The coefficient of correlation between carbon isotope value of methane ($\delta^{13}\text{C}_1$) and production time is $R^2 < 0.8$ (Fig. 8c). The coefficient of correlation of carbon isotope value of ethane ($\delta^{13}\text{C}_2$) was smaller than 0.5 (Fig. 8d).

According to the logarithmic relationship between the drying coefficient ($\text{C}_1/\text{C}_{1-5}$) and production time, we can establish a model of preliminary prediction regarding the total output of shale gas in a single well (Fig. 8). However, due to the limitations of real production and analytical data, some problems encountered in the physical production process must be solved before the establishment of an actual prediction model. For example, new gasses will be constantly mixed into shale gas in actual fracturing production process, hence, the drying coefficient and carbon isotope value of shale gas component in it are likely to not only simply decrease or increase but is largely related to fracturing times of shale, fracturing scope and shale gassiness in the researched area. Nonetheless, the general trend for drying coefficient and carbon isotope value of shale gas component is that they change with the change of production time and can fully reflect the change of shale gas content. Besides, much like in an actual formation, the shale temperature and pressure are remarkably different from onsite desorption condition that leads to a relatively low desorption degree of shale gas, thus, the drying coefficient minima generated by gas component fractionation

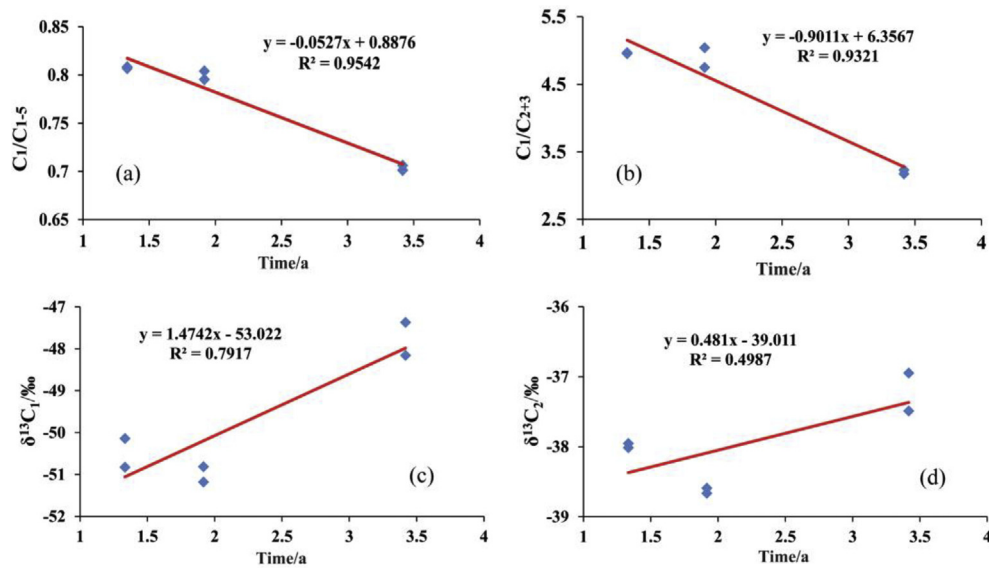


Fig. 8. Relationship between the drying coefficient, $\delta^{13}C_1$, and production time.

Table 2
Gas components characteristics of producing wells in the study area.

Sample	Gas components/%							C_1/C_{1-5}	C_1/C_{2+3}
	C_1	C_2	C_3	iC ₄	nC ₄	iC ₅	nC ₅		
LP177-1	67.01	14.67	6.07	2.14	2.32	1.37	1.29	0.71	3.23
LP177-2	66.43	14.77	6.16	2.11	2.45	1.11	1.69	0.70	3.17
YYP1-1	76.18	10.93	4.17	1.17	1.68	0.26	0.33	0.80	5.04
YYP1-2	75.69	11.51	4.42	1.20	1.59	0.31	0.43	0.80	4.75
YY13-1	77.40	9.91	5.71	0.95	1.22	0.31	0.41	0.81	4.96
YY13-2	77.49	9.85	5.75	0.89	1.14	0.32	0.42	0.81	4.97

in the production well needs to be further verified according to real production data.

4. Conclusions

(1) The CH₄ content in shale gas within the researched area is relatively low, whereas the drying coefficient (C_1/C_{1-5}) mainly ranges from 0.6 to 0.8, generally indicating that the shale gas drying coefficient of this area is low and that moisture dominates; these factors are heavily influenced by the adsorption/diffusion effect. The composition percentage of methane decreases constantly with the increasing desorption time, the content of heavy

- hydrocarbon component (C_{2+}) intensifies, and the gas drying coefficient decreases constantly by a great degree.
- (2) The logarithmic relation graph between the drying coefficient (C_1/C_{1-5} , C_1/C_{2+3}) and the desorbed gas amount per unit mass demonstrate a good correlation; the correlation coefficient is $R^2 > 0.8$. We can attempt to establish the prediction model of shale gas content according to the logarithmic relationship between gas component drying coefficient and desorbed gas amount per unit mass shale.
- (3) The desorption course of shale gas has an apparent effect on CH₄ and C₂H₆ carbon isotopic fractionation, and their carbon isotope values gain weight in varying degrees. Thereunto the weight gain degree of carbon isotope value of CH₄ is higher as much as 10‰.
- (4) The correlation between carbon isotope value of desorbed gas ($\delta^{13}C_1$, $\delta^{13}C_2$) and desorbed gas amount per unit mass is fairly bad with its correlation coefficient being $R^2 < 0.7$. For the reason that the thermal maturity of shale in the researched area is relatively low, the $\delta^{13}C_1$ is generally smaller than $\delta^{13}C_2$, and the “inverted sequence” phenomenon of carbon isotope does not appear.
- (5) The coefficient of the production time and gas drying coefficient in the different production wells was over 0.9, but the correlation between the carbon isotope value and

Table 3
Gas isotopic characteristics of producing wells in the study area.

Sample	Carbon isotope/‰							
	C_1	C_2	C_3	iC ₄	nC ₄	iC ₅	nC ₅	CO ₂
LP177-1	−47.37	−36.95	−32.74	−34.12	−31.81	−31.41	−32.19	−21.05
LP177-2	−48.16	−37.49	−32.96	−34.11	−31.95	−31.49	−32.18	−22.29
YYP1-1	−50.81	−38.66	−33.13	−34.63	−31.83	−7.90	−31.00	−12.34
YYP1-2	−51.18	−38.59	−33.11	−34.36	−31.85	−30.75	−32.20	−14.52
YY13-1	−50.14	−37.95	−32.74	−33.89	−31.70	−30.80	−32.31	−18.28
YY13-2	−50.83	−38.01	−32.86	−34.45	−31.77	−31.23	−31.90	−18.92

production time was comparatively inconsequential. The ultimate cumulative recovery of the production well can be preliminarily estimated according to the logarithmic association between the drying coefficient (C_1/C_{1-5}) and production time.

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Conflict of interest

The authors declare no conflict of interest.

References

- [1] Jian Li, Zhaolu Liu, Zhisheng Li, Qituan Yan, Xiuqing Shan, Che Ma, Experiment investigation on the carbon isotope and composition fractionation of methane during gas migration by diffusion, *Nat. Gas Geosci.* 14 (6) (2003) 463–468.
- [2] Hua Yang, Wenzheng Zhang, Chuanli Zan, Jun Ma, Geochemical characteristics of Ordovician subsalt gas reservoir and their significance for reunderstanding the gas source of Jingbian gasfield, east Ordos Basin, *Nat. Gas Geosci.* 20 (1) (2009) 8–14.
- [3] D. Leythaeuser, A. Mackenzie, R.G. Schaefer, M. Bjoroy, A novel approach for recognition and quantification of hydrocarbon migration effects in shale sandstone sequence, *AAPG Bull.* 68 (2) (1984) 196–219.
- [4] Jianfa Chen, Ping Shen, Baojia Huang, Qiming Zhang, Application of contents of chemical components and isotopic composition of oil-gas to research on the secondary migration of Ying-qiong basin in China, *J. Univ. Petrol., China* 24 (4) (2000) 91–94.
- [5] Qiang Wang, Xiaowen Fu, Zhiming Xu, Shouzhi Hu, Xiong Hu, Development and application of stable carbon isotopes in natural gas and oil geochemistry, *Nat. Gas Geosci.* 16 (2) (2005) 233–237.
- [6] T. Zhang, B. Krooss, Experimental investigation on the carbon isotope fractionation of methane during gas migration by diffusion through sedimentary rocks at elevated temperature and pressure, *Geochim. Cosmochim. Acta* 65 (2001) 2723–2742.
- [7] Jialan Lu, Jiamo Fu, Huizhi Zhang, Dehan Liu, Study on simulation of natural gas migration in different conditions, *Oil Gas Geol.* 12 (2) (1991) 153–160.
- [8] Wenhui Liu, Mengjin Chen, Ping Guan, Jianjing Zheng, Qiang Jin, Guoyi Hu, Yanqing Xia, Three-end-members Geochemical Tracing System of Natural Gas Generated and Reservoiring and Its Application, Gansu Science and Technology Press, Lanzhou, 2009, pp. 82–96.
- [9] Tongwei Zhang, Xianbing Wang, Jianfa Chen, Yali Wang, Chemical composition of gases as a geochemical tracer of natural gas migration, *Acta Sedimentol. Sin.* 17 (4) (1999) 627–631.
- [10] Huixi Lin, Fuqi Cheng, Qiang Jin, Fractionation mechanism of natural gas components and isotopic compositions and sample analysis, *Nat. Gas Geosci.* 22 (2) (2011) 195–200.
- [11] Fuqi Cheng, Qiang Jin, Composition and isotope fractionations of accumulated natural gas and their significance, *Nat. Gas Geosci.* 16 (4) (2005) 522–525.
- [12] B. Krooss, D. Leythaeuser, Experimental measurements of the diffusion parameters of light hydrocarbons in water-saturated sedimentary rocks, II. Results and geochemical significance, *Org. Geochem.* 12 (1988) 91–108.
- [13] E. Pernaton, A. Prinzhofer, F. Schneider, Reconsideration of methane signature as a criterion for the genesis of natural gas: influence of migration on isotopic signature, *Oil Gas Sci. Technol. Rev.* 51 (1996) 635–651.
- [14] S. Schloemer, B. Krooss, Molecular transport of methane, ethane and nitrogen and the influence of diffusion on the chemical and isotopic composition of natural gas accumulations, *Geofluids* 4 (2004) 81–108.
- [15] F. Richter, R. Mendybaev, J. Christensen, I.D. Hutcheon, R.W. Williams, N.C. Sturchio, A.D. Beloso Jr., Kinetic isotopic fractionation during diffusion of ionic species in water, *Geochim. Cosmochim. Acta* 70 (2006) 277–289.
- [16] X. Xia, Y. Tang, Isotope fractionation of methane during natural gas flow with coupled diffusion and adsorption/desorption, *Geochim. Cosmochim. Acta* 77 (2012) 489–503.
- [17] A. Fux, Experimental evidence against an appreciable isotopic fractionation of methane during migration, *Organ. Geochem.* 12 (1996) 725–732.
- [18] B. Gunter, Isotope fractionation during gas chromatographic separations, *J. Chromatogr. Sci.* 9 (1971) 191–194.
- [19] J. Lu, E. Toti, C. Rebecca, Carbon isotope effects of methane transport through Anahuac Shale—a core gas study, *J. Geochem. Explor.* 148 (2015) 138–149.
- [20] Hui Han, Dahua Li, Yong Ma, Lijun Cheng, Lin Qi, Qi Wang, Ningning Zhong, The origin of marine shale gas in the northeastern Sichuan Basin, China: implications from chemical composition and stable carbon isotope of desorbed gas, *Acta Pet. Sin.* 34 (3) (2013) 453–459.
- [21] Jianbo Zhang, Mingxin Tao, Geological significances of coal bed methane carbon isotope in coal bed methane exploration, *Acta Sediment. Sin.* 18 (4) (2000) 611–614.
- [22] Honglin Liu, Hongyan Wang, Guoliang Zhao, Guizhong Li, Application of coal bed methane stable carbon isotope in exploration of coal bed methane field, *J. Xi'an Univ. Sci. Technol.* 24 (4) (2004) 442–446.
- [23] Lijiang Duan, Shuheng Tang, Honglin Liu, Baocun Zhu, The impact of coal reservoir physical properties on carbon isotope fractionation of coal bed methane, *Acta Geol. Sin.* 82 (10) (2008) 1330–1334.
- [24] Gang Gao, Guangdi Liu, Xulong Wang, Yueqian Zhang, Yuhua Kong, Daomin Zhang, Jin Gao, Characteristics of separated shale gas from the upper triassic of Junggar Basin, *Nat. Gas Geosci.* 24 (6) (2013) 1284–1289.
- [25] Yan Du, Bo Yu, Min Xu, Geochemical characteristics of shale gas from Yanchang formation in Southeastern Yishan slope, *J. Xi'an Univ. Sci. Technol.* 35 (1) (2015) 63–71.
- [26] Zhongyuan Zhao, Chiyang Liu, Zhanli Ren, Geology of petroliferous basins and their systematic engineering in research, *Oil Gas Geol.* 27 (1) (1990) 108–113.
- [27] Zaiyi Tian, Qingchun Zhang, Lithofacies Palaeogeography and Hydrocarbon Characteristics of Chinese Oil and Gas Basins, Petroleum Industry Press, Beijing, 1997, pp. 369–377.
- [28] Suizheng Yang, Wenhua Jin, Zhenhong Li, Multicycle superimposed basin form and evolution of Ordos Basin, *Nat. Gas Geosci.* 17 (4) (2006) 494–498.
- [29] W.J. Stahl, Carbon isotope fractionations in natural gases, *Nature* 251 (1974) 134–135.
- [30] B. Gunter, J. Gleason, Isotope fractionation during gas chromatographic separations, *J. Chromatogr. Sci.* 9 (1971) 191–192.
- [31] B. Tilley, S. Mclellan, S. Hiebert, B. Quartero, B. Veilleux, K. Muehlenbachs, Gas isotope reversals in fractured gas reservoirs of the western Canadian Foothills: mature shale gases in disguise, *AAPG Bull.* 95 (8) (2011) 1399–1422.
- [32] X. Xia, J. Chen, R. Braun, Y. Tang, Isotopic reversals with respect to maturity trends due to mixing of primary and secondary products in source rocks, *Chem. Geol.* 339 (2013) 205–212.